

Applicants: Donald R. Huffman, et al.

Serial No. 08/471,890

Docket: 7913ZY

Filing Date: June 7, 1995

Examiner: S. Hendrickson

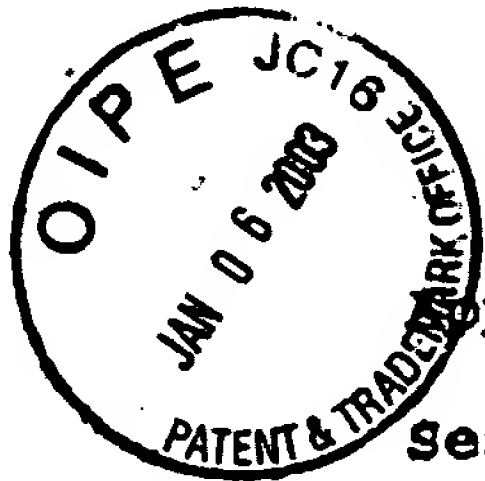
Group Art Unit: 1754

Title: SUPPLEMENTAL DECLARATION OF DONALD R. HUFFMAN UNDER 37  
C.F.R. §1.131 Dated May 10, 2000

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**TC 1700**



PATENT  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Donald R. Huffman, et al. Examiner: P. DiMauro

Serial No.: 08/486,669

Art Unit: 1754

Filed: June 7, 1995

Docket: 7913ZAZYX

For: NEW FORM OF CARBON

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JAN 08 2003

TC 1700

Assistant Commissioner for Patents  
Washington, DC 20231

SUPPLEMENTAL DECLARATION OF DONALD R. HUFFMAN  
UNDER 37 C.F.R. §1.131

Sir:

I, Donald R. Huffman, declare and say as follows:

1. I am a co-applicant of the above-identified application.

2. The other co-inventor of the above-identified application is Wolfgang Kratschmer, with whom I have collaborated. Although Dr. Kratschmer conducted his research at the relevant time at the Max Planck Institute in Germany, during the course of our collaboration, we have regularly communicated with one another, exchanging ideas, concepts and experimental details and results. In addition, we have visited each other's laboratories and have conducted additional research therein during our visits relating to the subject matter of the present invention described in the above-identified application. All of our combined activities have led to the completion of the invention described and claimed in the above-identified application.

3. I am currently a Regent's Professor of Physics, at the University of Arizona. I have received several accolades and awards relating to the subject invention, which include, inter alia, a Material Research Society Annual Medal Award in 1993, which I shared with Dr. Kratschmer, for the "Discovery of a Way to Produce Macroscopic Quantities of the Fullerenes and for Ellucidating (sic) Many of the Physical and Chemical Properties", and the Hewlett-Packard EuroPhysics Prize in 1994, which I shared with Drs. Kratschmer, Smalley and Kroto, for the "Discovery of New Molecular Forms of Carbon and their Production in the Solid State".

My curriculum vitae which lists, inter alia, my awards and honors and publications, is attached hereto as Exhibit A. (Exhs. A-1 to A-8).

4. It is my understanding that the United States Patent and Trademark Office cited a paper by Kratschmer, et al. published in Chemical Physics Letters, 1990, 167-170 ("Kratschmer, et al.") in support of a rejection of the above-identified application.

5. It is my understanding that Kratschmer, et al. published on July 6, 1990.

6. The invention described and claimed in the above-identified application was completed in the United States prior to July 6, 1990, i.e., the publication date of Kratschmer, et al.

7. The present invention is directed to a method of producing fullerene-60 and fullerene-70 as species of fullerenes in macroscopic amounts. An integral part of the present invention comprises vaporizing elemental carbon, e.g., graphite, in the presence of an inert quenching gas under conditions effective to form a soot comprising fullerenes, e.g., fullerene-60, which species of fullerenes are present in the sooty carbon product in macroscopic amounts. Proving that macroscopic amounts of fullerene species, e.g., fullerene-60, are present in the soot required isolation of the same from the soot. Thus, in addition to the step of producing species of fullerenes, e.g. fullerene-60, in macroscopic amounts, much of the activity described hereinbelow focused on proving that the species were produced in macroscopic amounts. Thus, we undertook to isolate fullerene-60 and fullerene-70, as species of fullerenes, from the soot.

8. As evidence that these acts, including the completion of the present invention in the U.S., occurred prior to the publication of Kratschmer et al., annexed hereto and made a part hereof are Exhibits B-I consisting of photocopies of laboratory records of experiments conducted in the laboratories at the University of Arizona.

9. The acts reported in the laboratory notebook entries were conducted prior to July 6, 1990, the publication date of Kratschmer, et al. either by myself or by someone working under my direction and control.

10. Data not pertinent to this invention and dates have been masked out in the preparation of these photocopies.

11. To enhance the understanding of the present process as to the acts described herein, reference is made to Exhibit B, which is a photocopy of 4 pages from Dr. Lowell Lamb's laboratory notebook, identified as Pages B-1 to B-4. Dr. Lamb, at the relevant time, was a graduate student working in my laboratory under my supervision and control.

12. Exhibit B summarizes in detail an embodiment of the present invention for producing fullerene species, e.g., fullerene-60, in macroscopic amounts. It describes that graphite rods are vaporized in an inert atmosphere of helium, e.g., 100 torr of helium, in a belljar apparatus. Above the rods is a chimney made out of a 2" diameter quartz tube topped with two microscopic slides to collect the vaporized carbon smoke. The carbon smoke is scraped off the chimney and sides of the chamber, and placed in benzene. The benzene is evaporated off until a brownish gold residue remains, then the brownish gold residue is sublimed in an atmosphere of inert gas such as helium. The sublimed material is collected on a quartz substrate. In each of the instances wherein the product was isolated, it was produced in amounts that could be seen with the naked eye.

13. One product of the procedure described hereinabove in paragraph 12 is a relatively pure fullerene-60 molecule in macroscopic amounts. This is verified by the UV-

VIS spectrum, in which one observes a camel structure in the absorption pattern, e.g., three specific absorptions at about 220, 270 and 340nm in the UV. Since the absorption between 240 and 270 nm reminded us (Kratschmer and myself) of camel humps, we designated the spectra as camel humps. (The three absorptions turned out to be associated with and is reflective of the presence of fullerene-60 and fullerene-70 in the sample).

14. An example of such a spectrum is depicted on pages B-3 and B-4, which are photocopies of additional pages in Lowell Lamb's notebook. Although the spectra are in color in the notebooks, the colors did not reproduce in the original photocopying. I have therefore retraced the lines with the appropriate colors on these pages of the exhibit and have written the appropriate color designations above and/or below the lines.

15. In the experiments described hereinbelow, the sooty carbon product was obtained by following the procedure outlined hereinabove. The emphasis in these experiments was to definitely prove that macroscopic amounts of fullerene species, e.g., fullerene-60, were produced. Thus, the emphasis in many of the exhibits is to separate the product produced in accordance with the procedure described herein from the soot and to show by measuring physical characteristics, such as UV spectra, IR spectra, X-ray diffraction pattern, and the like that the present process produced species of fullerenes, e.g.,

fullerene-60 and that they were produced in macroscopic amounts.

16. In the experiment described on pages B-3 and B-4, Lamb had followed the procedure described hereinabove and prepared fullerene species, e.g., fullerene-60, from soot, as described in paragraph 12. He had separated the fullerene products from the carbon sooty product by sublimation. More specifically, he had sublimed the mixed fullerene products, containing, among other things, fullerene-60 and fullerene-70, from the soot, prepared in accordance with the procedure described in Paragraph 12 herein in a helium atmosphere until a thin film was formed on the surface of the quartz substrate. According to the procedure described therein, he removed the film from the quartz substrate and took the UV spectra of the collected material. As outlined in the notebook he continued subliming the material in the soot until another film appeared, which, he again isolated and scanned. He repeated this process until no more material was collected on the quartz substrate. It is noted that in the spectrum located on the right side of Page B-3, there are blue and red lines which show absorption at about 230, 270 and 340 nm. These absorptions turned out to be associated with and reflective of the presence of fullerene-60 and fullerene-70 in the sample. This again is illustrated by the blue and the red lines in the spectra located on the left side on page B-4.

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one atmosphere of helium. The quartz substrate was placed just above the crucible for collecting the sublimed material. To prove that I had prepared the fullerene-60 in macroscopic amounts, I performed several sublimations and scanned the sublimed product each time. A typical UV is provided on Page C-9.

21. The UV spectra on page C-9 clearly shows the presence of the camel humps, and this clearly indicates that fullerene-60 was produced by the process described hereinabove.

22. Exhibit D is a photocopy of two pages of a laboratory notebook of Lowell Lamb. The sooty carbon product comprising macroscopic amounts of fullerene-60 was prepared as above. The isolation of a fullerene species, e.g., fullerene-60, from carbon soot and the purification of same, was effected by sublimation. Attached to the bottom of Page D-1 and Page D-2 is the UV and visible spectra, respectively, of the fullerene-60 product so obtained.

23. On the graph on the bottom of Page D-1, attention is drawn to the UV absorptions at 240, 270 and 340nm again indicating the presence of fullerene-60 in the sample.

24. Exhibit E is a photocopy of three pages of Lowell Lamb's laboratory notebook. Page E-1 is a visible spectra of fullerene-60, prepared in accordance with the procedure described hereinabove and shows absorption at about 415, 500, and 670nm, which is indicative of fullerene-60.

Page E-2 describes modifications of the procedure described on Page 92 and 93 of the notebook (Pages B-1 and B-2). Moreover, it refers to an IR spectrum of fullerene-60 on NaCl produced in accordance with the procedure outlined on Pages B-1 and B-2. It refers to the absorption of the fullerene-60 at 1410 and 1180 cm., which turns out to be associated and reflective of the presence of fullerene-60. Page E-3 is a copy of IR spectra of fullerene-60 on NaCl referred to on Page E-2.

25. Exhibit F is a photocopy of relevant portions of a progress report which was written in Lowell Lamb's laboratory notebook. Page F-3 comments on the IR and UV spectra of the fullerene-60 sample obtained and reports that the procedure described in Exhibit B produces a fullerene-60 product in approximately 0.1 gram batches.

26. The fullerene products, produced in accordance with the procedure described hereinabove, were soluble in non-polar solvents and insoluble in polar solvents. This is indicated in Exhibit G, which is a photocopy of two pages of my notebook.

27. Exhibit G consists of two pages, Page G-1 and G-2. Page G-1 describes the tests which I conducted regarding determining the solubility of the fullerene product. I found that it is soluble in benzene, CS<sub>2</sub> and CCl<sub>4</sub>, but insoluble in water, acetone, methanol and propanol.

28. The fact that the fullerene product is found to be soluble in non-polar solvents, while the soot was insoluble in the non-polar solvent was evidence that non-polar solvents could be used to extract the fullerene product from the soot. Thus, this represented an alternate means for separation of the fullerene product from the soot.

29. Page G-2 is the UV/VIS spectrum of the fullerene product dissolved in benzene.

30. The spectra referred to in paragraphs 21 and 29 are of exceptional quality and clearly show the presence of fullerene-60.

31. Exhibit H consists of one page and is an X-ray diffraction of the fullerene powder produced in accordance with the procedure described hereinabove. The spectrum is identical to the ones we and others published with respect to fullerene-60.

32. Exhibit I, consisting of one page, is a mass spectrum of the fullerene material produced in accordance with the procedure described hereinabove. It clearly shows the presence of two species of fullerenes, e.g., fullerene-60 (mass 720) and fullerene-70 (mass 840) in a single ionization, along with some breakup products of fullerene-60 such as doubly ionized fullerene-60.

33. These exhibits demonstrate that a process for the preparation and isolation of various fullerene species, e.g., fullerene-60 and fullerene-70 as species of fullerenes,

in macroscopic amounts has been performed by myself or under my direct supervision and control in the United States prior to the publication date of Kratschmer et al.

34. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated:

May 10, 2000

Donald R. Huffman  
DONALD R. HUFFMAN

MJC:ahs/bb

PUBLICATIONS  
(not including published abstracts and contributed papers)

1. D.R. Huffman and M.H. Norwood, "Specific Heat and Elastic Constants of Calcium Fluoride at Low Temperatures," *Phys. Rev.* **117**, 709 (1960).
2. D.R. Huffman, R.L. Wild, and J. Callaway, "Optical Properties of Alpha-MnS in the Fundamental Absorption Region," *J. Phys. Soc. Japan* **215**, 623 (1966); and Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, 1966.
3. D.R. Huffman and Robert L. Wild, "Specific Heat of MnS through the Neel Temperature," *Phys. Rev.* **148**, 526 (1966).
4. D.R. Huffman and Robert L. Wild, "Optical Properties of Alpha MnS," *Phys. Rev.* **156**, 989 (1967).
5. D.R. Huffman, "Total Intensities of Some Crystal Field Transitions in MnO and MnS Related to the Antiferromagnetism," 1968 Conference on Magnetism and Magnetic Materials, *J. Appl. Phys.* **40**, 1334 (1969).
6. D.R. Huffman, R.L. Wild, and M. Shinmei, "Optical Absorption Spectra of Crystal Field Transitions in MnO," *J. Chem. Phys.* **50**, 4092 (1969).
7. D.R. Huffman, "A Possible Cause of Some Unidentified Interstellar Absorption Bands: Crystal Field Absorption Bands Due to  $\text{Fe}^{3+}$ ," *Astrophys. J.* **161**, 1157 (1970).
8. D.R. Huffman, "An Explanation for the Broad Supernovae Bands," *Nature* **225**, 833 (1970).
9. D.R. Huffman and J.L. Stapp, "Interstellar Silicate Extinction Related to the 2200 A Band," *Nature* **229**, 45 (1971).
10. K.L. Day and D.R. Huffman, "Measured Extinction Efficiency of Graphite Smoke in the Region 1200-6000 A," *Nature Physical Science* **243**, 50 (1973).
11. Arlon J. Hunt, T.R. Steyer, and D.R. Huffman, "Infrared Surface Modes in Small NiO Particles," *Surface Science* **36**, 454 (1973).
12. Arlon J. Hunt and D.R. Huffman, "A New Polarization-Modulated Light Scattering Technique for Determining the Elements of the Scattering Matrix," *Rev. Sci. Instrum.* **44**, 1753-1782 (1973).
13. D.R. Huffman and J.L. Stapp, "Optical Measurements on Solids of Possible Interstellar Importance," in *Interstellar Dust and Related Topics*, ed. Greenberg and van de Hulst (1973).

14. T.R. Steyer, K.L. Day, and D.R. Huffman, "Infrared Absorption by Small Amorphous Quartz Spheres," *Appl. Opt.* **13**, 1586 (1974).
15. K.L. Day, T.R. Steyer, and D.R. Huffman, "A Quantitative Study of Silicate Extinction," *Astrophys. J.* **191**, 415 (1974).
16. D.R. Huffman, "Optical Properties of Particulates," *Astrophys. and Space Sci.* **34**, 175 (1975); invited paper presented at the Symposium on Solid State Astrophysics, Cardiff, Wales.
17. A.J. Hunt and D.R. Huffman, "A Polarization-Modulated Light Scattering for Determining Liquid Aerosol Properties," *Japanese Journal of Applied Physics* **14**, 435 (1975).
18. W.S. Bickel, J.F. Davidson, D.R. Huffman, and R. Kilson, "Application of Polarization Effects in Light Scattering: A New Biophysical Tool," *Proceedings of the National Academy of Sciences* **73**, 486 (1976).
19. T.P. Martin, R. Merlin, D.R. Huffman, and M. Cardona, "Resonant Two Magnon Raman Scattering in Alpha-Fe<sub>2</sub>O<sub>3</sub>," *Solid State Commun.* **22**, 565-567 (1977).
20. D.R. Huffman, "Interstellar Grains: The Interaction of Light with a Small-Particle System," *Advances in Physics* **26**, 126-230 (1977).
21. Roger J. Perry, Arlon J. Hunt, and Donald R. Huffman, "Experimental Determinations of Mueller Scattering Matrices for Nonspherical Particles," *Appl. Opt.* **17**, 2700-2710 (1978).
22. W. Krätschmer and D.R. Huffman, "Infrared Extinction of Heavy Ion Irradiated and Amorphous Olivine with Applications to Interstellar Dust," *Astrophys. and Space Sci.* **61**, 195 (1979).
23. D.R. Huffman and C.F. Bohren, "Effect of Shape on Strong Infrared Absorption Bands of Artificial Aerosols," in *Proceedings of the Workshop on Artificial Aerosols*, Vail, Colorado, June 19-20, 1979.
24. D.R. Huffman and C.F. Bohren, "Infrared Absorption Spectra of Non-spherical Particles Treated in the Rayleigh Ellipsoid Approximation," in *Light Scattering by Irregularly Shaped Particles* (Plenum, 1980), pp. 103-112.
25. D.R. Huffman and R. Trykozko, "Reflectance and Optical Constants of CdIn<sub>2</sub>Se<sub>4</sub> Crystals," *J. Appl. Phys.* **52**, 5283 (1981).
26. D.R. Huffman, L.A. Schwalbe, and D. Schiferl, "Use of Smoke Samples in Diamond-Anvil Cells to Measure Pressure Dependence of Optical Spectra: Application to the ZnO Exciton," *Sol. State Commun.* **44**, 521 (1982).

27. S. Twomey and D.R. Huffman, "Workshop Review," in **Light Absorption by Aerosol Particles**, eds. H.E. Gerber and E.E. Hindman (Spectrum Press, 1982).
28. D. R. Huffman, "Optical Absorption Studies of Surface Plasmons and Surface Phonons in Small Particles," **Festkorperprobleme (Advances in Solid State Physics) XXIII**, 49-75 (1983).
29. C.F. Bohren and D.R. Huffman, **Absorption and Scattering of Light by Small Particles**, (Wiley, New York, 1983) 530pp.
30. K.P. Pflibsen and D.R. Huffman, "Electronic and Vibrational Spectra of AgNa Molecular Clusters and Small Particles," **Surface Science** **156**, 793 (1985).
31. W. Krätschmer, N. Sorg, and D.R. Huffman, "Spectroscopy of Matrix-Isolated Carbon Cluster Molecules Between 200 and 850 nm Wavelength," **Surface Science** **56**, 814 (1985).
32. C.F. Bohren and D.R. Huffman, **Authorized Russian Translation of Absorption and Scattering of Light by Small Particles**, (1986).
33. D.R. Huffman, "The Applicability of Bulk Optical Constants to Small Particles," in **Optical Effects Associated with Small Particles**, eds. P. Barber and R.C. Chang (World Scientific, 1987).
34. Donald R. Huffman, "Methods and Difficulties in Laboratory Studies of Cosmic Dust Analogues," in **Experiments on Cosmic Dust Analogues**, eds. E. Bussoletti et al. (Kluwer, 1988).
35. Donald R. Huffman, "Report of the Working Group on Carbon," in **Experiments on Cosmic Dust Analogues**, eds. Bussoletti et al. (Kluwer, 1988).
36. Donald R. Huffman, "The Applicability of Bulk Optical Constants to Small Particles," in **Optical Effects Associated with Small Particles**, eds. P. Barber and R.C. Chang (World Scientific Press, 1988), 279-324.
37. Willem P. Van der Mewre, Donald R. Huffman, and Burt V. Bronk, "Reproducibility and Sensitivity of Polarized Light Scattering for Identifying Bacterial Suspensions," **Appl. Opt.** **28**, 5052 (1989).
38. Donald R. Huffman, "Pitfalls in Calculating Scattering by Small Particles," in **Interstellar Dust**, eds. L.J. Allamandola and A.G.G.M. Tielens (Kluwer, Boston, 1989), 329.
39. Joe Kurtz and Donald R. Huffman, "Simultaneous Infrared and uv-visible Absorption Spectra of Matrix-isolated Carbon Vapor," in **Interstellar Dust**, eds. L.J. Allamandola and A.G.G.M. Tielens (Kluwer, Boston, 1989), 71.
40. W. Van de Merwe, D. Huffman, and B. Bronk, "Establishing a Standard for Polarized

Light Scattering in Bacteria," in **Proceedings of the Eleventh International Conference on Lasers**, 1989.

41. David M. Roessler and Donald R. Huffman, "The Optical Properties of Magnesium Oxide," in **Handbook of Optical Constants of Solids, Volume II**, ed. E.D. Palik (Academic Press, N.Y.) 1990.
42. D.R. Huffman, C. Weidman, and S. Twomey, "Repetition of Danjon Earthshine Measurements of Determination of the Long Term Trends in Earth's Albedo," **Colloque Andre Danjon, Journees 1990**, eds M. Capitaine and M. Debarbat, (Paris Observatory Publ., Paris, 1990) p. 71.
43. W. Krätschmer, K. Fostiropoulos, and D.R. Huffman, "Search for the UV and IR Spectra of C<sub>60</sub> in Laboratory-Produced Carbon Dust," in **Dusty Objects in the Universe**, eds. E. Bussoletti and A.A. Cittone (Kluwer, Dordrecht), 1990.
44. W. Krätschmer, K. Fostiropoulos, and D.R. Huffman, "The Infrared and Ultraviolet Absorption Spectra of Laboratory-produced Carbon Dust: Evidence for the Presence of the C<sub>60</sub> Molecule," *Chem. Phys. Lett.* **170**, 167-170 (1990).
45. Joe Kurtz and Donald R. Huffman, "Simultaneous Infrared and Uv-visible Absorption Spectra of Matrix-isolated Carbon Vapor," *J. Chem. Phys.* **92**, 30-35, (1990).
46. W. Krätschmer, Lowell D. Lamb, K. Fostiropoulos, and Donald R. Huffman, "Solid C<sub>60</sub>: A New Form of Carbon," *Nature* **347**, 354-358 (1990).
47. Henry Ajie, Marcos M. Alvarez, Samir J. Anz, Rainer D. Beck, Francois Diederich, K. Fostiropoulos, Donald R. Huffman, W. Krätschmer, Yves Rubin, Dilip Sensharma, and Robert L. Whetton, "Characterization of the Soluble All-Carbon Molecules C<sub>60</sub> and C<sub>70</sub>," *J. Chem. Phys.* **94**, 8630-8633 (1990).
48. J.L. Wragg, J.E. Chamberlain, H.W. White, W. Krätschmer, and Donald R. Huffman, "Scanning Tunneling Microscopy of Fullerite (C<sub>60</sub> & C<sub>70</sub>)," *Nature* **348**, 623 (1990).
49. C.I. Frum, Rolf Engleman, Jr., Hartmut G. Hedderich, Peter Bernath, Lowell D. Lamb, and Donald R. Huffman, "The Infrared Emission Spectrum of Gas Phase C<sub>60</sub> (Buckminsterfullerene)," *Phys. Chem. Lett.* **176**, 504-508 (1991).
50. D.L. Lichtenberger, K. W. Nebesny, C. D. Ray, L. D. Lamb, and D. R. Huffman, "Valence and Core Photoelectron Spectroscopy of C<sub>60</sub>, Buckminsterfullerene," *Chem. Phys. Lett.* **176**, 203-208 (1991).
51. K. Sinha, J. Menendez, G.B. Adams, J.B. Page, O.F. Sankey, L.D. Lamb, and D.R. Huffman, "Raman study of icosahedral C<sub>60</sub>," in **SPIE Vol. 1437, Applied Spectroscopy in Material Science**, 1991.

52. Donald R. Huffman and Wolfgang Krätschmer, "Solid C<sub>60</sub> -- How We Found It," in **Clusters and Cluster Assembled Materials**, Vol. 206, Averbach, R.S., et al, eds., Materials Research Society, Pittsburgh, 1991.
53. G.B. Adams, J.B. Page, O.F. Sankey, K. Sinha, J. Menendez, and D.R. Huffman, "First principles molecular dynamics study of the molecule C<sub>60</sub>," *Phys. Rev. B (Rapid Communications)* **44**, 4052 (1991).
54. D.L. Lichtenberger, M.E. Jatcko, K.W. Nebesney, C.D. Ray, D.R. Huffman, and L.D. Lamb, "The ionization of C<sub>60</sub> in the gas phase and in thin solid films," in **Clusters and Cluster Assembled Materials**, eds. R.S. Averbach et. al., Mat. Res. Soc. Proc. **206** (1991).
55. S.G. Kukolich and D.R. Huffman, "EPR Spectra of C<sub>60</sub> Anion and Cation Radicals," *Chem. Phys. Lett.* **182**, 263 (1991).
56. D. Sarid, T. Chen, S. Howells, M. Gallagher, L. Yi, D.L. Lichtenberger, K.W. Nebesney, C.D. Ray, D.R. Huffman, and L.D. Lamb, "Buckyball-substrate interactions probed by STM and AFM," **ULTRAMICROSCOPY: Proceedings Volume of STM '91**, eds. P. Descouts and H. Siegenthaler (Elsevier, Amsterdam, 1991), in press.
57. J. Mort, K. Okumura, M. Machonkin, R. Ziolo, D.R. Huffman, and M.I. Ferguson, "Photoconductivity in solid films of C<sub>60</sub>/C<sub>70</sub>," *Lett.* **186**, 281-283 (1991).
58. J. Mort, R. Ziolo, M. Machonkin, D.R. Huffman, and M.I. Ferguson, "Electrical conductivity studies of undoped solid films of C<sub>60</sub>/C<sub>70</sub>," *Chem. Phys. Lett.* in press (1991).
59. D.R. Huffman, "Sold C<sub>60</sub>," *Phys. Today* **44**, No. 11 (1991).60. H.E. Schaefer, M. Forster, R. Wurschum, W. Krätschmer, and D.R. Huffman, "Positron lifetime and annihilation site in C<sub>60</sub>/C<sub>70</sub> fullerites," *Mat. Sci. Forum* **105-110**, 815-820 (1992).
61. W. Krätschmer and D.R. Huffman, "Fullerites: New forms of crystalline carbon," *Carbon* **30**, 1143 (1992).
62. J. Mort, M. Machonkin, R.F. Ziolo, D.R. Huffman, and M.I. Ferguson, "Temperature dependence of photoconductivity in buckminsterfullerene films," *Appl. Phys. Lett.* **60**, 1735-1737 (1992).
63. H.E. Schaefer, M. Forster, R. Wurschum, W. Krätschmer, and D.R. Huffman, "Positrons as probes in C<sub>60</sub> fullerites," *Phys. Rev.* **B43**, 12164 (1992).
64. T. Chen, S. Howells, M. Gallagher, D. Sarid, L.D. Lamb, D.R. Huffman, and R.K. Workman, *Phys. Rev. (Rapid Communications)* **B45**, 14411 (1992).
65. L.D. Lamb, D.R. Huffman, R.K. Workman, S. Howells, T. Chen, D. Sarid, and R. Ziolo,

"Extraction and STM imaging of spherical giant fullerenes," *Science* **255**, 1413 (1992).

66. D. Sarid, T. Chen, S. Howells, M. Gallagher, L. Yi, D.L. Lichtenberger, K.W. Nebesney, C.D. Ray, D.R. Huffman, and L.D. Lamb, "Buckyball-substrate interactions probed by STM and AFM," *Ultramicroscopy* **42-44**, 610 (1992).

67. S. Seraphin, D. Zhou, J. Jiao, L.D. Lamb, and D.R. Huffman, "High resolution TEM of fullerenes of different sizes," *Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America*, 298 (1992).

68. S. Howells, T. Chen, M. Gallagher, D. Sarid, D.L. Lichtenberger, L.L. Wright, C.D. Ray, D.R. Huffman, and L.D. Lamb, "High resolution images of isolated C<sub>60</sub> molecules on gold (111) using scanning tunneling microscopy," *Surf. Sci.* **274**, 141 (1992).

69. R.F. Ziolo, E.P. Giannelis, B.A. Weinstein, M.P. O'Horo, B.N. Ganguly, V. Mehrotra, M.W. Russell, and D.R. Huffman, "Matrix-mediated synthesis of nanocrystalline gamma-Fe<sub>2</sub>O<sub>3</sub>: A new optically transparent magnetic material," *Science* **257**, 219-223 (1992).

70. M.E. Lin, R.P. Andres, R. Reifengerger and D.R. Huffman, "Electron emission from an individual, supported C<sub>60</sub> molecule," *Phys. Rev. B* **47**, in press.

71. L.D. Lamb, J.D. Lorentzen, and D.R. Huffman, "A light-scattering method for determining the composition of particles on surfaces," in *Particles on Surfaces 4: Detection, Adhesion, and Removal*, K.L. Mittal, ed., (Marcel Dekker, New York) in press (1994).

72. M.J. Gallagher, D. Chen, B.P. Jacobsen, D. Sarid, L.D. Lamb, F.A. Tinker, J. Jiao, D. R. Huffman, S. Seraphin, and D. Zhou, "Characterization of carbon nanotubes by scanning probe microscopy," *Surface Science Letters* **281**, L335-L340 (1993).

73. S.W. McElvaney, J.H. Callahan, M.M. Ross, L.D. Lamb, and D.R. Huffman, "Large odd-numbered carbon clusters from fullerene/ozone reactions," *Science* **260**, 1632-1634 (1993).

74. L.D. Lamb and D.R. Huffman, "Fullerene production," *J. Phys. Chem. Sol.* **54**, 1635-1643 (1993).

75. L. Nemes, R.S. Ram, P.F. Bernath, F.A. Tinker, M.C. Zumwalt, L.D. Lamb, and D.R. Huffman, "Gas phase infrared emission spectra of C<sub>60</sub> and C<sub>70</sub>: Temperature dependent studies," *Chem. Phys. Letters* **218**, 295-303 (1994).

76. D.R. Huffman and W. Krätschmer, "From interstellar dust to fullerenes," **Proceedings of the International Workshop on Fullerenes and Atomic Clusters**, St. Petersburg, Russia, 4-9 Oct., 1993 (in press).
77. D.R. Huffman, "Synthesis and properties of fullerenes," in **Nanostructured Materials - Synthesis, Properties and Uses**, A.S. Edelstein & R.C. Cammarata, eds., (IOP, Techno House, Bristol, in press, 1994).
78. M.C. Zumwalt and D.R. Huffman, "Fullerene and polycyclic aromatic hydrocarbons," in **Recent Advances in Chemistry and Physics of Fullerenes and Related Materials**, K.M. Kadish & R.S. Ruoff, eds. (The Electrochemical Society, Pennington N.J., in press, 1994).
79. D.R. Huffman, "Applications of fullerenes," **Materials Letters** 21, 127 (1994).
80. Lowell D. Lamb, Donald R. Huffman, and J.D. Lorentzen, "A Light Scattering Method for Determining the Composition of Particles on Surfaces," in **Particles on Surfaces**, K.L. Mittal, ed., (Marcel Dekker, New York, 1995).
81. D. R. Huffman, "Fullerene Soot: What is It? What's in It?," **Molecular Materials** 7, 11-16 (1996).
82. D.R. Huffman and J.E. Fischer, "Remarks -- Physics of Fullerenes," **Molecular Materials** 8, 181 (1996).
83. Donald R. Huffman, "Fullerene Soot: Then and Now," in **The Chemical Physics of Fullerenes: 10 (and 5) Years Later**, W. Andreoni, ed., (Kluwer, Boston, 1996) 37-47.
84. R. Hitzemberger, H. Giebl, A. Berner, H. Puxbaum, A. Kasper, and D. Huffman, "Cloud Condensation Nuclei (CCN) Measurements at a Remote Continental Station in Central Europe (Mt. Sonnblick Observatory: Austria), reference ? not on the reprint. (1996).

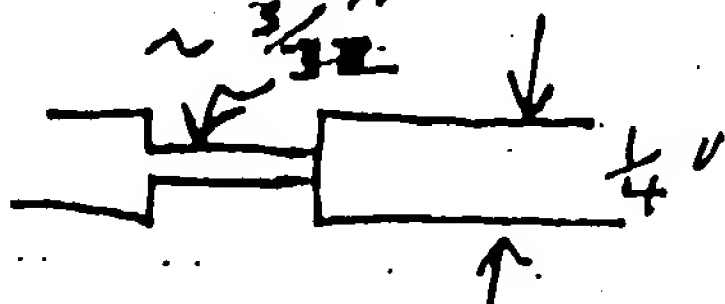
#### PATENTS

1. D.R. Huffman and Robin J. Robinson, "Method of Separation of Helium from Other Constituents of Natural Gas," U.S. Patent No. 3,239,996, granted March 15, 1966.
2. Donald R. Huffman and Lowell Lamb, "Aerogel/fullerene hybrid materials for energy," U.S. Patent No. 5,698,140, granted December 16, 1997.
3. Donald R. Huffman and W. Kratschmer, "Solid C<sub>60</sub>: A New Form of Carbon," Composition of Matter and Production Patents Filed 27 August 1990. (European patents granted, U.S. Patent Pending).

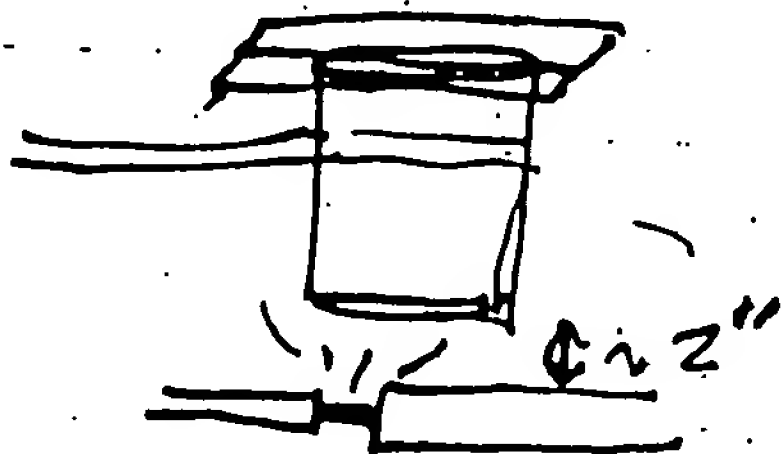
# Journal Entry

In the last three days, I've made some progress in the production of  $C_{60}$ . Below is the process.

- ① Evaporate Carbon in  $\sim 100$  Torr of  $He$ . The tip dimensions are



Above the rods I have a "chimney" made out of a  $\sim 2$ " diameter quartz tube topped with two microscope slides to collect the smoke



(\* Flush 3 times with  $\sim 100$  Torr of  $He$ , First

Set the variac to  $\sim 75$ ; if the tip breaks at ~~two~~ thin sections connect the  $1/4$ " rods, turn the voltage to 85.

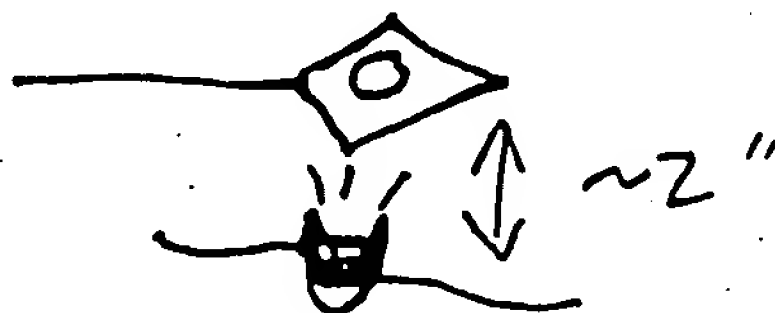
- ② Repeat  $\sim 5$  times.
- ③ Scrape smoke off chimney + sides of chamber.
- ④ Combine smoke + benzene in a test tube. Stir thoroughly.
- ⑤ Ultrasonic for  $\sim 2$  min.
- ⑥ Centrifuge on 4 for  $\sim 10$  min.
- ⑦ Pour Dark red liquid into quartz crucible - place crucible on warm hot plate (cool enough to be touched for a few seconds) and heat until all benzene has evaporated. A brownish golden residue should remain.

READ BY JAMES J. EMMETT

for 2 E

EXH. B-1

- (8) Put crucible with residue into wire basket in vacuum chamber.
- (9) Flush 3 times with 100 Torr of He - At 100 Torr of He, sublime  $C_{60}$  onto quartz substrate at  $\sim 30$  V on Variac until film appears on substrate.



- (10) Remove substrate + scan from 400-200 nm.
- (11) Clean substrate and Repeat (7) & (10) until all of the other volatiles have been driven off. This will have happened when the spectrum resembles the brown spectrum taped in on page 94. The blue and purple spectra are of samples which still contain this unknown volatile. What remains in the crucible is  $C_{60}$ .

### Temperature Dependence

Four  
Taped in on page 95 are ~~three~~ scans of a  $C_{60}$  sample

- (1) Blue - Room Temperature
- (2) Green - Immediately after immersion + equilibration in liquid  $N_2$ .
- (3) Purple - 2nd  $N_2$  Temp scan
- (4) Red - Final Room Temp scan.

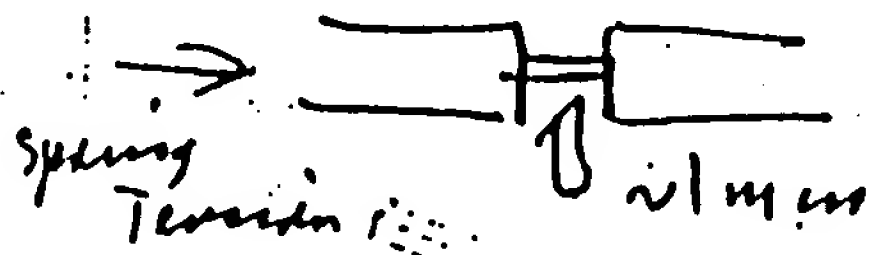
Broad feature (features?) in visible around  
425 - 525 nm appear real.

READ BY JOHN T. EMERY  
for Z. E. D.

# Co making

REDACTED

10:40 AM - Temp  $\approx 100^{\circ}\text{C}$   $\pm 380^{\circ}\text{F}$  as gauge  
according to calibration in Lowell's notebook



#1 UV spectrum on Cary 118 shows  
a good Co spectrum just as in and before.

Peak OD  $\approx 1.4$

Scraped off with sand blasted glassine paper.

#2 UV spectrum shows similar result

Peak OD  $\approx 2.25$ . At this production I predicted the  
data to allow the usual result of low temperature  
stuff to come off & disappear

Used samples #1 & #2 scraped off to try to sublimate Co.



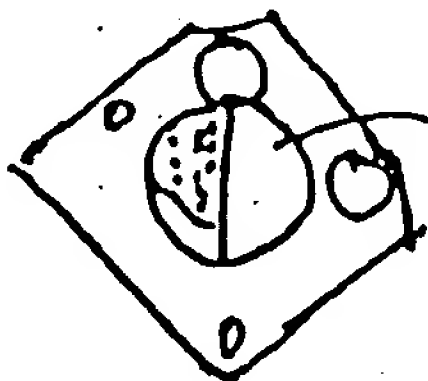
Multistandard tension wire coil placed carefully into a shape  
that would hold a clear quartz crucible.

Notes to about Co on surface & then something, just



blue by scattered light in darkness  
reddish outer ring

UV spectrum is uncharacteristic better background is seen



wipe off right side of sample  
to try to do part of clean vs dirty

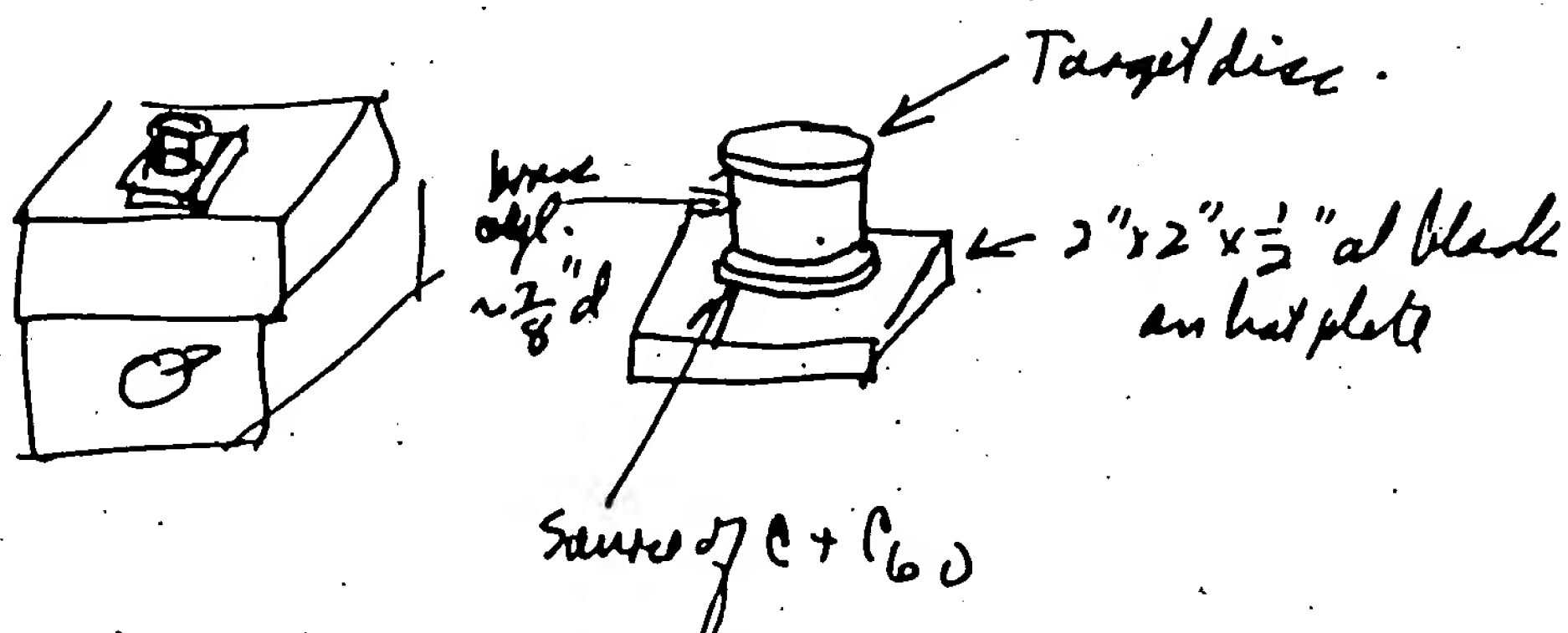
(cont.)

74

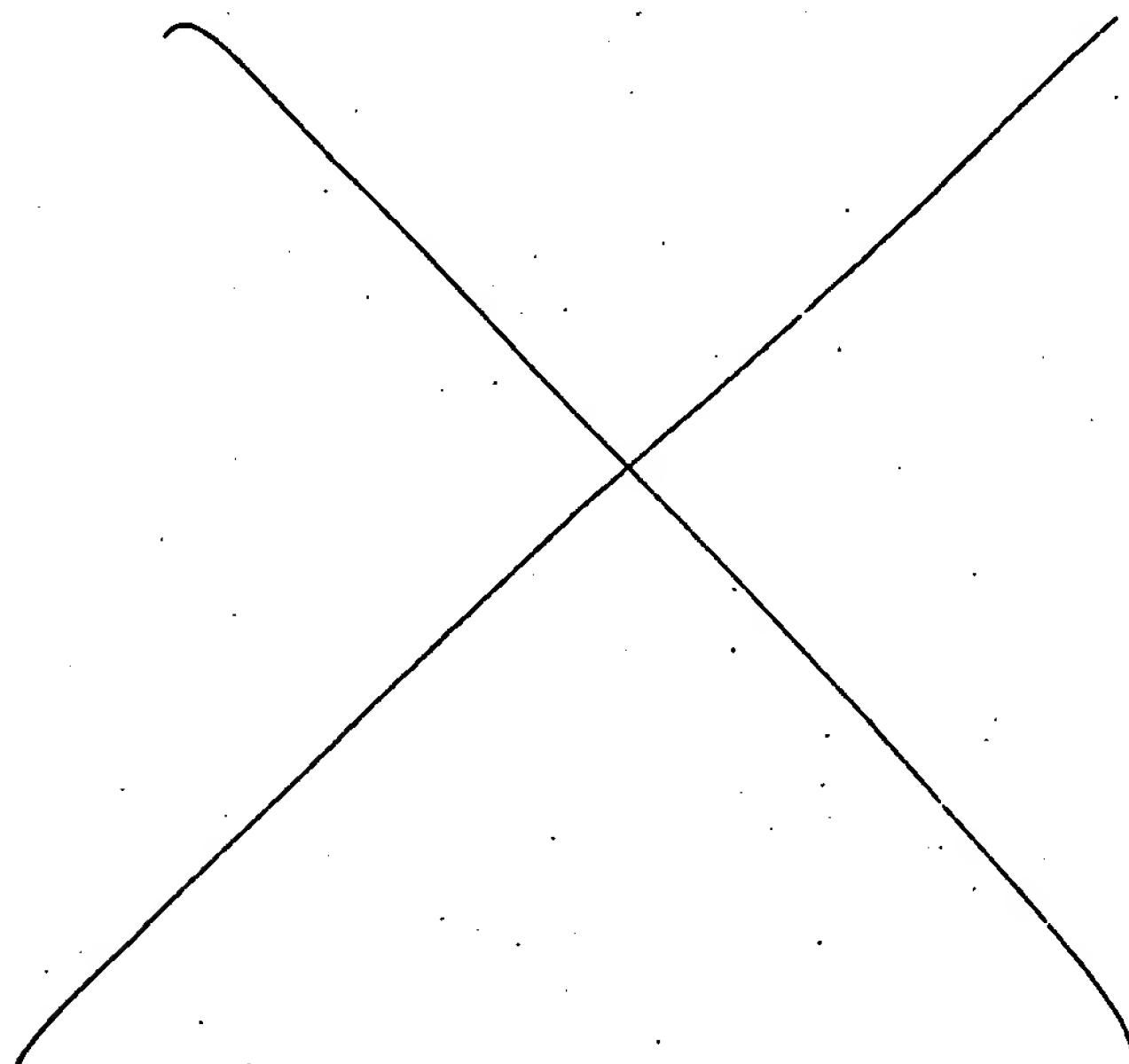
REDACTED

(cont.)

Attempt at Sublimation of  $C_{60}$  in Air  
on Hot Plate.



Heated for 10 min in the above arrangement. No indication of anything on target disc. Re-analysis of UV spectrum of source disc shows change away from  $\pi$  bump structure.



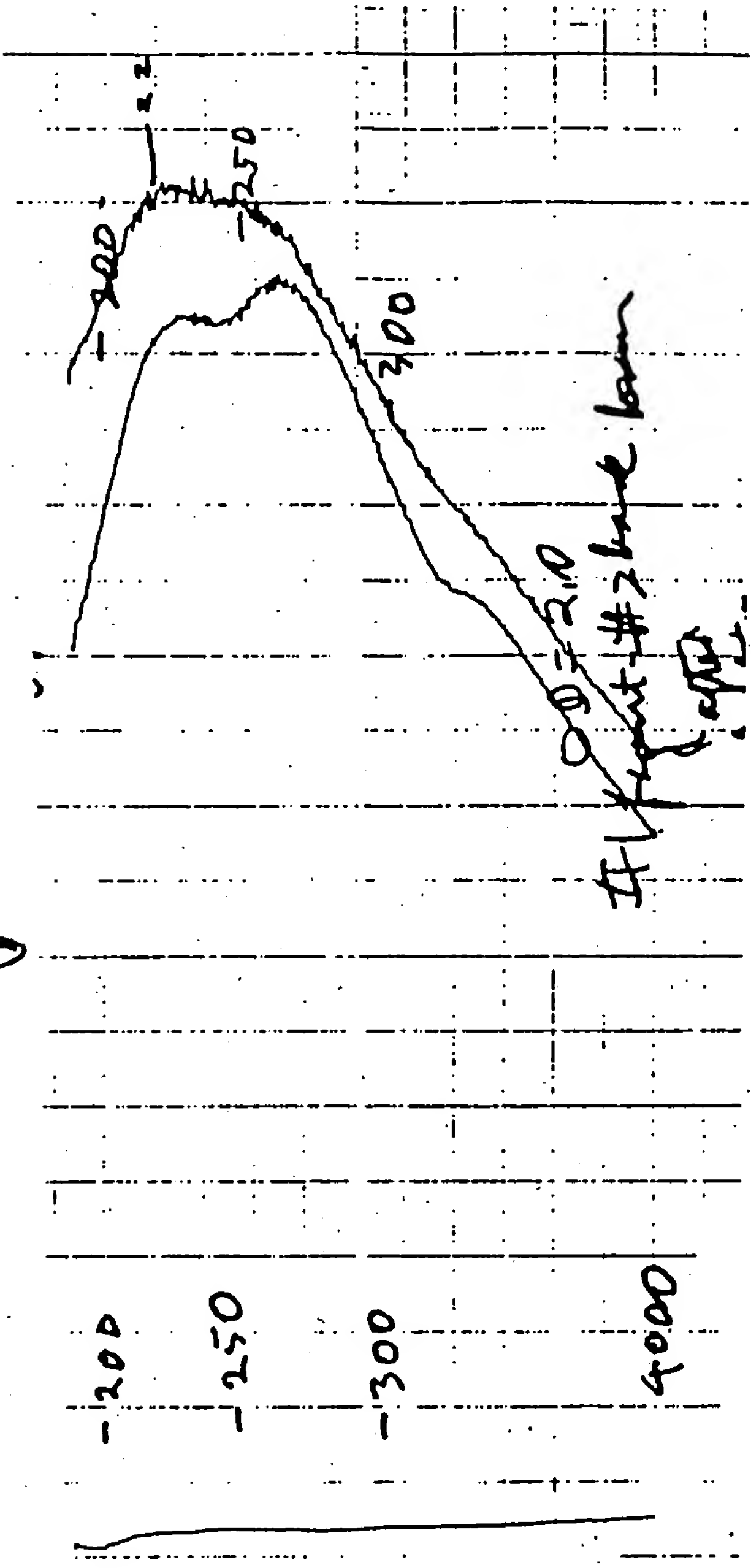
EXH. C-2

See next page

REDACTED

75

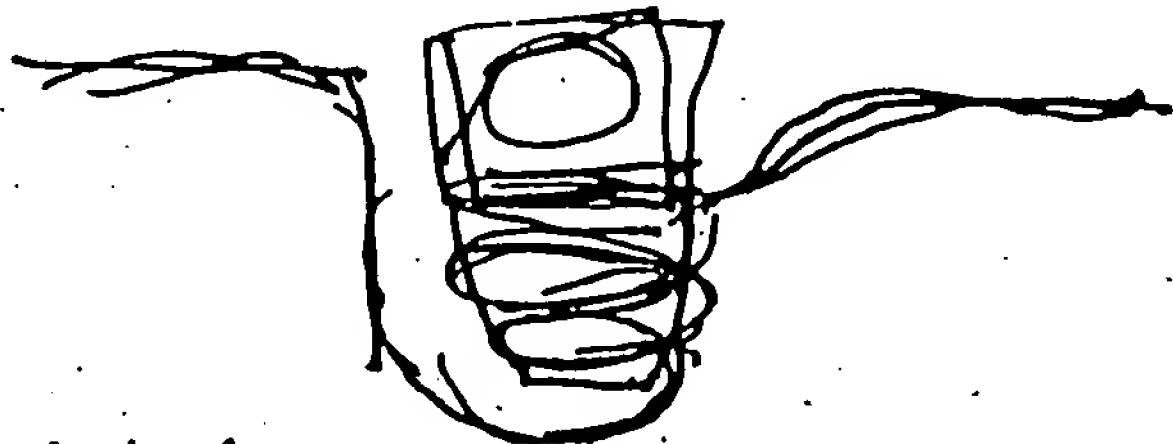
(cont.)



76

(cont.)

For next try at analyzing  $\text{CO}$  I wound a new coil around the dense quartz crucible out of 3-stranded tungsten.



Placed ab. holder with silica disc just above the crucible. Note: perspective of drawing above is not good.

Scraped carbon off the sample holder from a previous run -- also collected same by scraping from posts and other hardware in the chamber.

Flushed chamber w/  $\text{He}$  & filled to  $\sim \frac{3}{4}$  atm. Heated filament  $\sim 15$  amp until I observed something on disc.

Spectrometer opposite page shows that I indeed succeeded in concentrating  $\text{CO}$ .

The sample again appeared bluish by scattered light in the forward direction and perhaps reddish by transmission. Not what some flakes of the fluffy carbon that seems to have marked the surface.

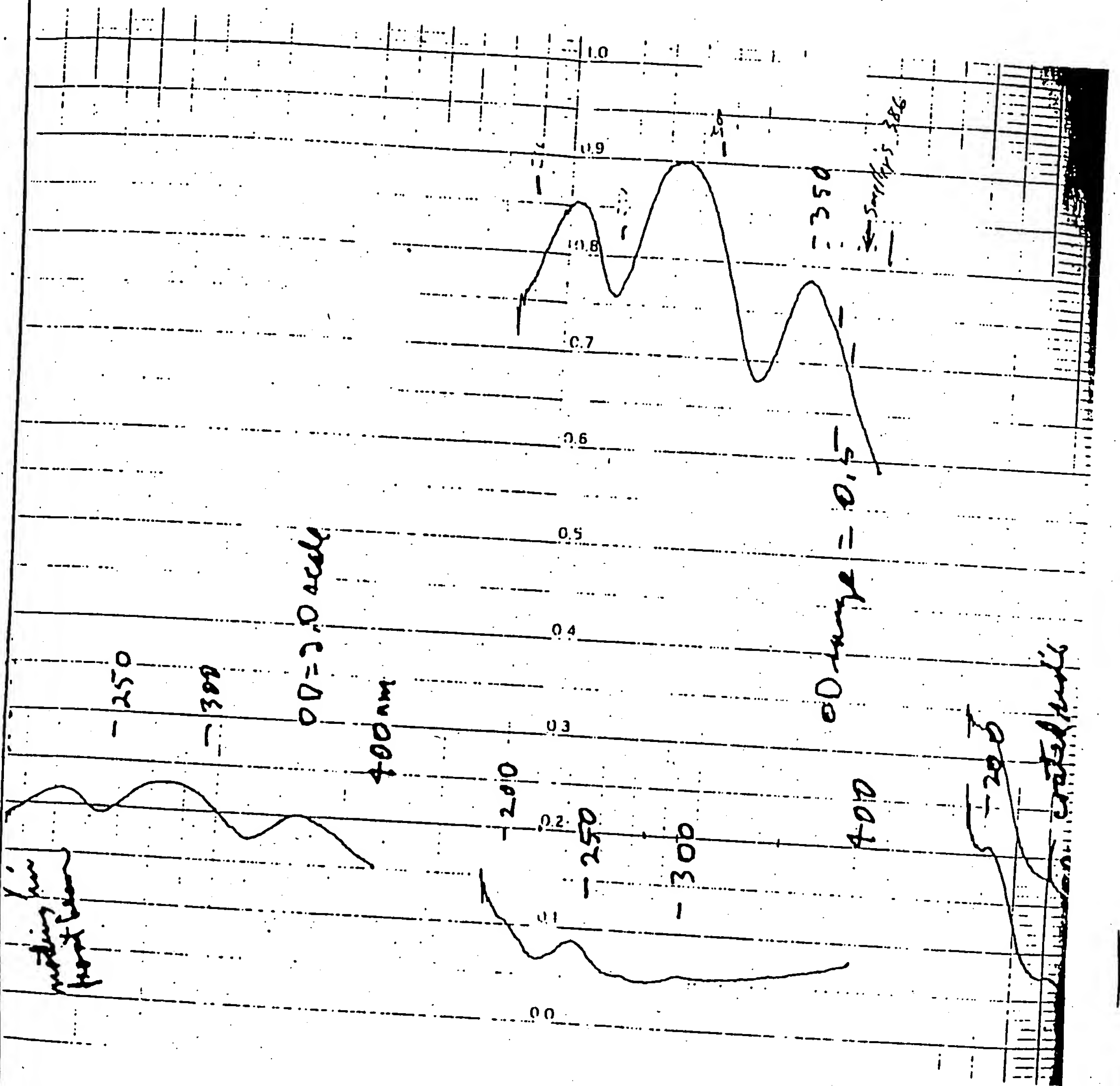
I will try to get around this by not scraping off the carbon into fluffy aggregates.



Fluffy carbon

REDACTED

77

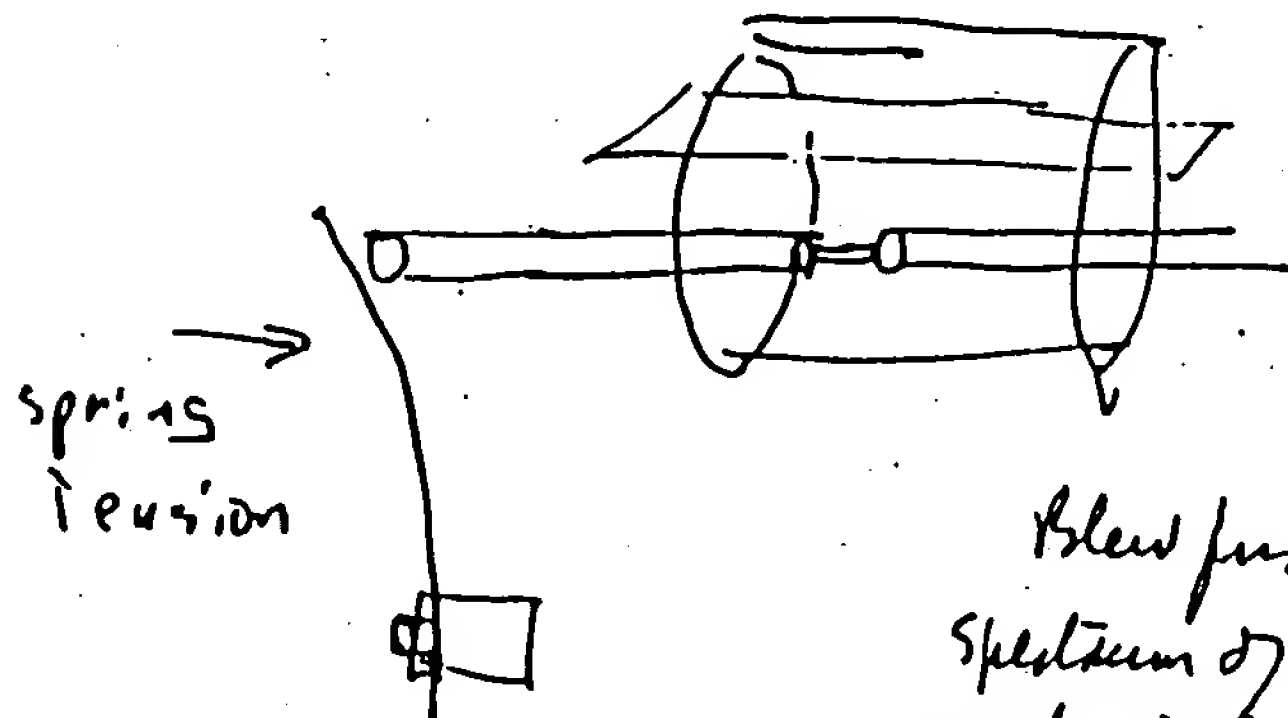


EXH. C-5

78

# More C<sub>60</sub> making

#1 Trial 3mm diameter rod in qtz. tube w/ microscope glass as shown below:



3mm is  
Blow from star cage.  
Spectrum of stuff inside shows  
material C<sub>60</sub> signature.

## #2 Trial

Same ring as above but 1 1/2 in dia. rod, a little longer than usual (~1cm). Rod snapped when heating started but smoke continues as shockwave part was pushed by spring expanded stop.

Heavy coating on inside of ring & on slide. Will try again with a 1.5mm x ~8mm tip to get more C<sub>60</sub>. Then try to concentrate it.

## #3 Trial

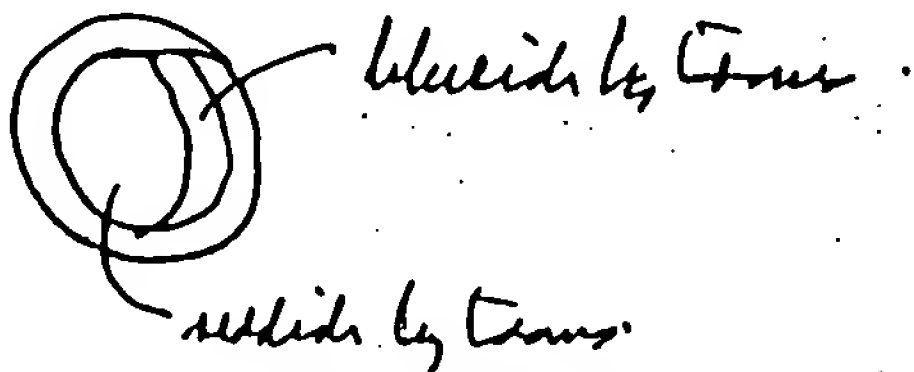
Heated rather quickly. Tip collapsed. ~5 sec in all to try to prevent draining off the C<sub>60</sub>.

#4 Microscope slide from #2-3 with heavy coating is broken into a few pieces to fit into crucible. Idea is to try to prevent the fluffy contaminant from yesterday by subliming directly from coated slide.



cont.

Heated filament to ~ 10 amp on meter. Filament misbehavior.  
 Heating most lenses distorted. Later settled down as that emission  
 and heating occurred. 40 amp on meter - 20 on current meter.  
 Left it for ~ 3 min while I observed deposition using  
 microscope light from above.



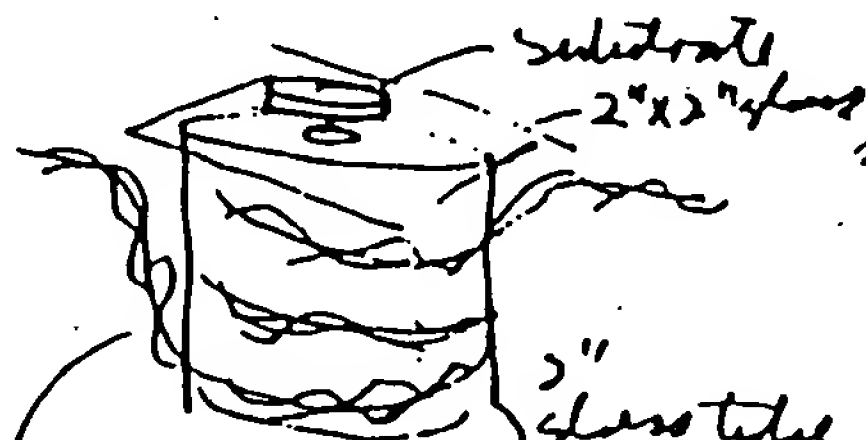
Two spots resulted. Two spectrum peaks. Totally different.  
 Don't understand the bluish by trans. part.

Cleaned substrate - will now try same charge as done on  
 bottom) to see if any  $\text{Co}$  is left:

Card. 3 min - 30v - 12.5 amp on primary  
 Apparent to some extent of smoke cloud present & stable  
 in chamber as viewed by microscope. Chamber cleaned in  
 darkened room. No evidence of any more  $\text{Co}$  at anything that  
 depositing on substrate.

Now try an unheated portion (4cm x 1cm) of heavily  
 coated microscope slide (#1 & #2). Increased power more  
 gradually. at 26.5v & 11 amp primary current I see spots of  
 coating develop on substrate. Also observe smoke in the chamber.

Now try the large (2") cylinder with heavy coat wire



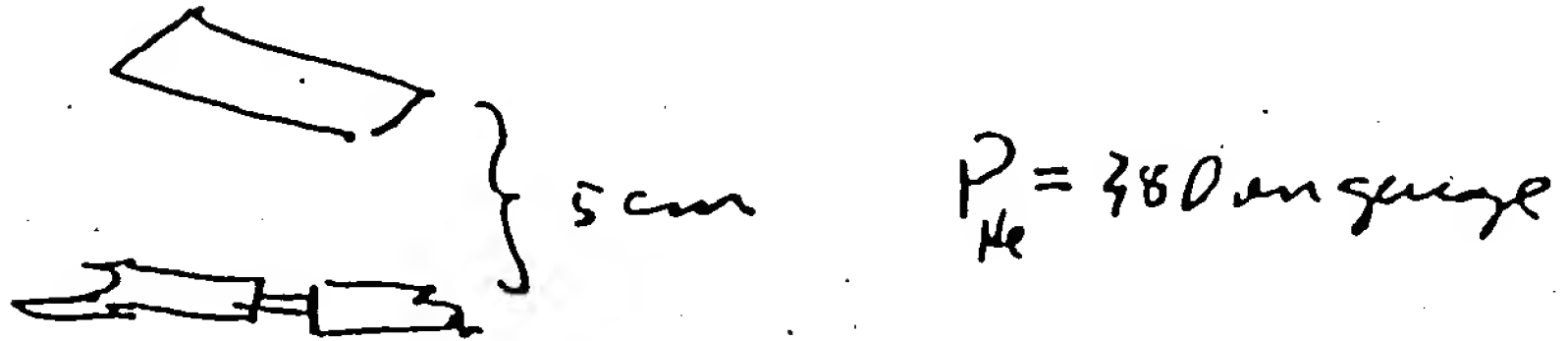
Various spectra on charts.

at 12.5 amp on filament  
 started getting coating on substrate

Results - Nothing got thru the  $\frac{1}{4}$ "  
 hole in 2x2 glass to substrate.  
 2"x2" have same coating of bluish & red.

80

Try Standard Condition to make heavy 60 amols.

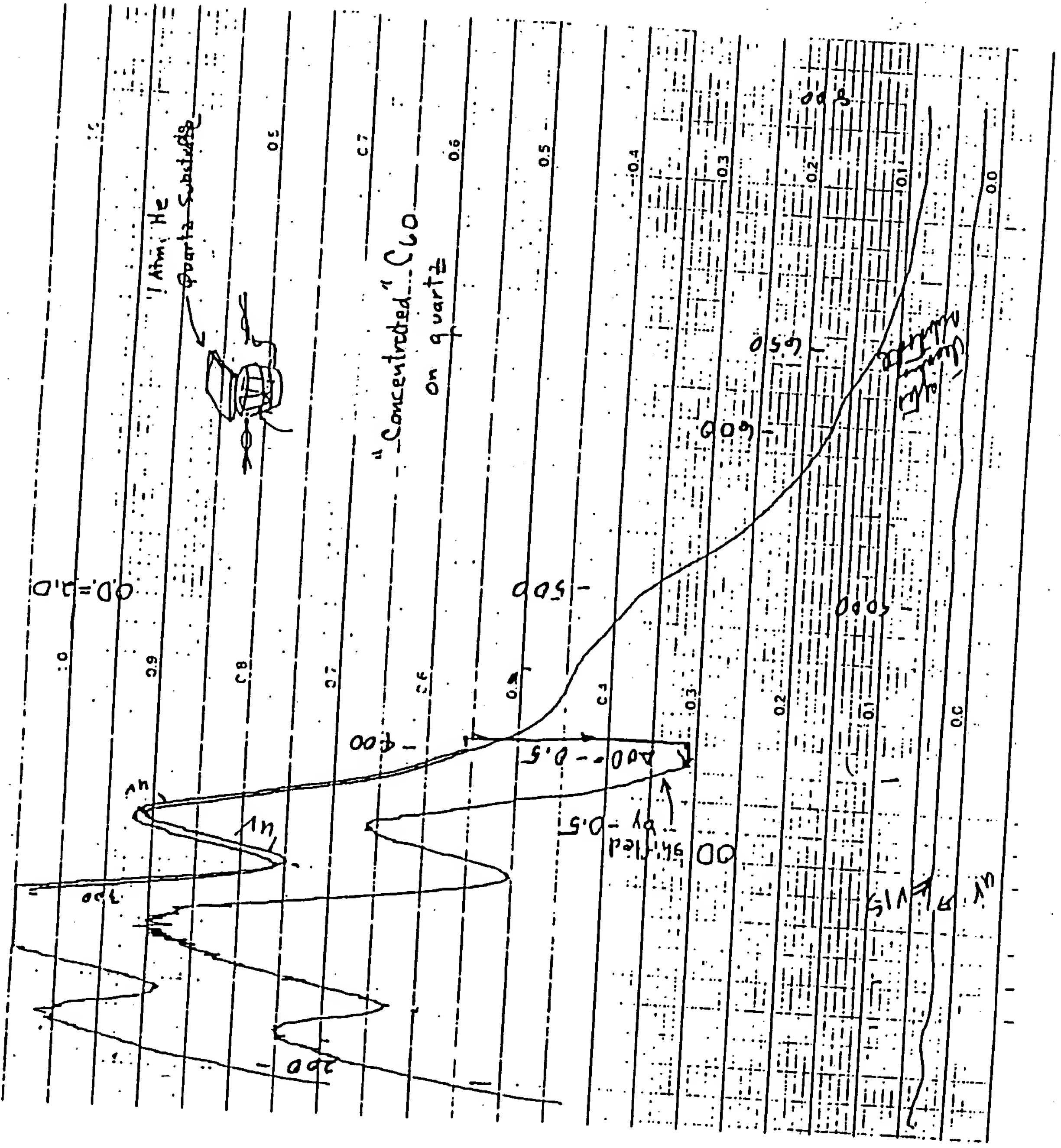


Today I Faxed to Wolfgang a copy of the spectrum of  
 JH which ~~is~~ a copy is shown on the attached page.

There appears to be structure in the region between about  
 4500 Å and 7000 Å which is real. The curve of  
 course shows why the material is reddish brown.

To W. Krialschmer

Spectrum of  
"concentrated" smoke

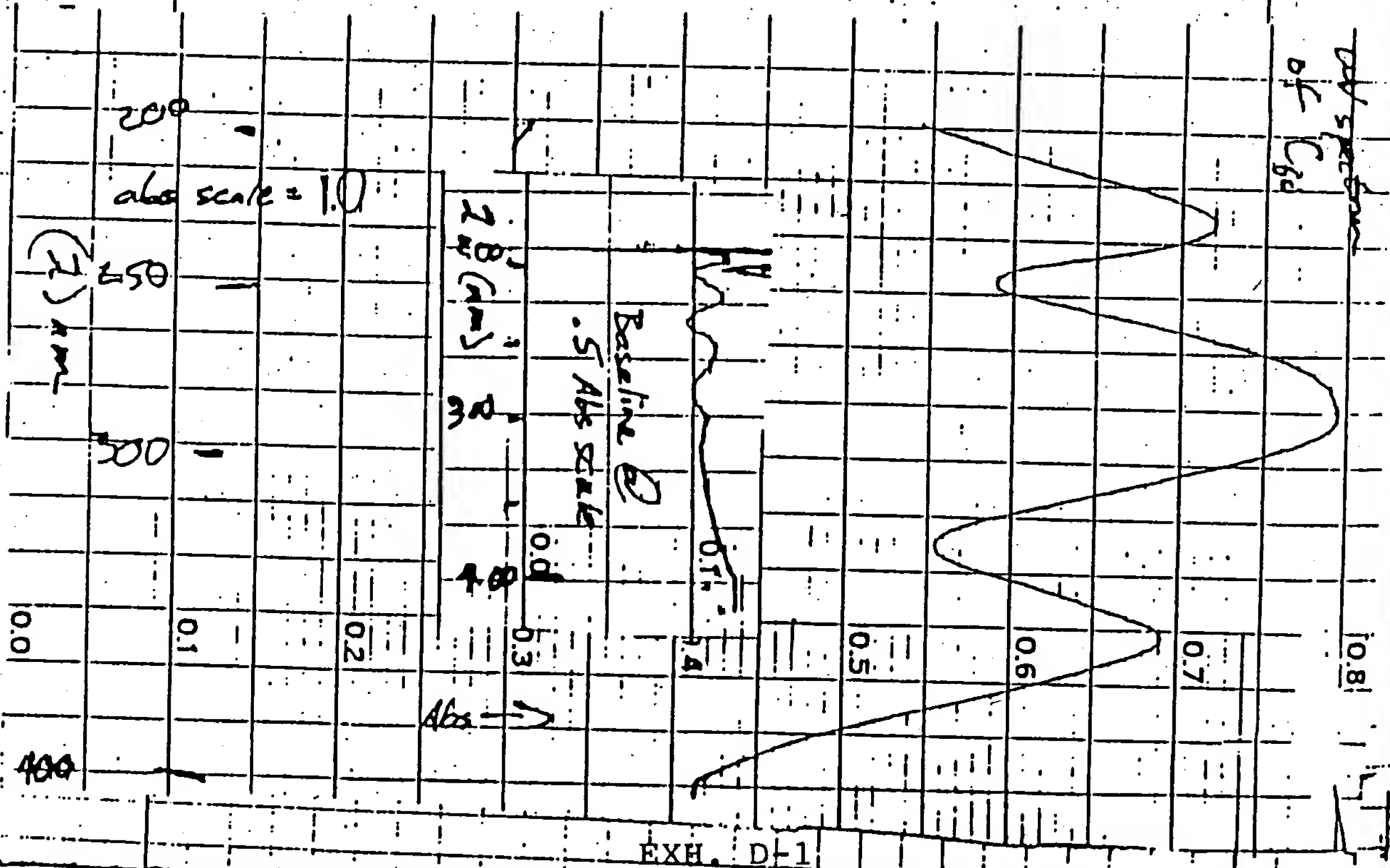


C<sub>60</sub>

Today I made smoke + concentrated C<sub>60</sub> using sublimation.  
Taped in below is the UV scan of the sample,  
and taped in on page 91 is the Visible scan.

There appear to be 4 absorption features superimposed  
on the broad carbon feature in the visible. The 620 nm  
and 730 nm may be instrumental error (see baseline).  
The 445 and 495 are close to the 4428 Å and  
4882 nm DIB. !!!

The spectra



*The Sun*

REDACTED

Visible Spectrum of  $C_{60}$

0.9

Baseline @ .5 abs scale

400

500

600

700

445

475

-blue

0.5

0.4

620

0.3

730

0.2

0.1

0.0

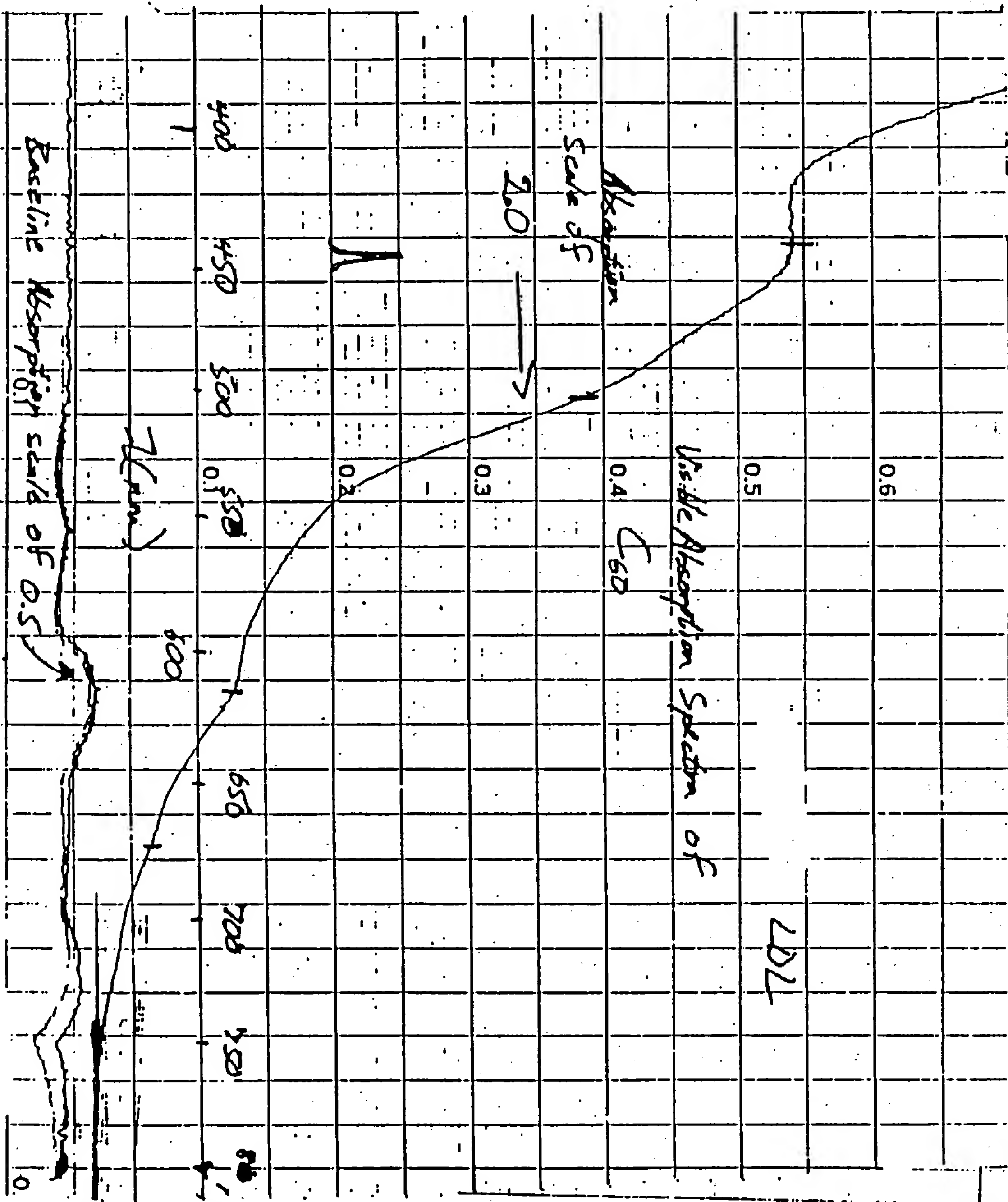
400

500

600

$\lambda$  (nm)

Taped in below is a visible spectrum of  $C_{60}$ .  
 I see features at 445, 500, 670, and possibly 620 nm.  
 These may correspond to the 4428, 4882, 6660, and 6200 Å  
 DIB.



~~Modifications~~ Modifications to Smoke Production Method on pages 92-93.

Step ① - Tip diameter  $\sim \frac{1}{8}$ "

Step ② - Substrate-Crucible separation  $\sim 2$  mm

### Questions

① Why am I only seeing some of the DIB's? Specifically, why am I not seeing the 5800 Å feature?

#### Answer A

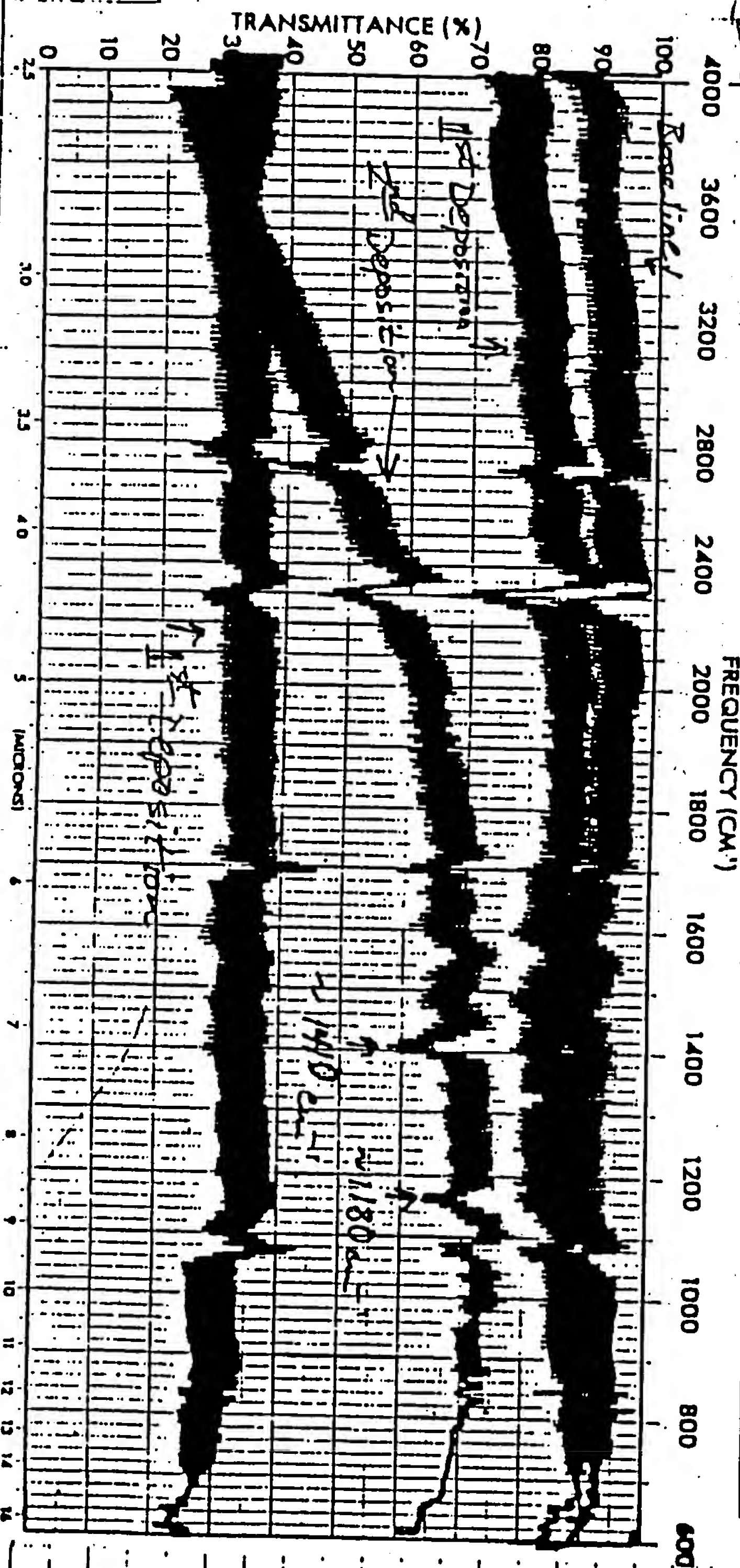
I am only seeing pure carbon and/or carbon 60 with a trapped He feature. The other DIB's are due to  $C_{60}$  with various ions trapped inside.

#### Answer B

The other DIB's are due to  $C_{70}$ ,  $C_{92}$ , ...

Taped in on page 98 is an IR scan of  $C_{60}$  on NaCl. Careful comparison of the baseline to the absorption spectrum shows only two features - at  $\sim 1410$  &  $1180$   $\text{cm}^{-1}$ . These match up well to the Krättschmer et al features at ~~1429~~ 1429 and  $1183$   $\text{cm}^{-1}$ . In *Nature* this morning, he states that they are still seeing contamination due to C-H at  $2900$   $\text{cm}^{-1}$ . I don't see that in my spectrum, so either it is not present or the instrument is not sensitive enough.

REDACTED

IR spectra of  $C_{60}$  on NaCl

REDACTED

Progress Report

REDACTED

#### IV UV-Visible

I have obtained good spectra of  $C_{60}$  from about 200-700 nm using the CARY 118. Scans are typed in on pages 90, 91, 96. I see visible features at 445, 500, 670, and possibly 620 nm.

#### V IR Spectra

An IR scan from 4000-800  $cm^{-1}$  is typed in on page 98. I see the two features at 1429 and 1183  $cm^{-1}$  and no other features. There seems to be relatively little contamination.

#### VI Near IR

Using the CARY 14, I've made some preliminary scans from 600-1600 nm. There is really only one candidate feature - at 1280 nm - but I don't have a baseline yet.

#### VIII $C_{60}$ Production

The most important thing I've done is refine our method for  $C_{60}$  production. I would estimate that we are now able to make it in ~0.1 gram batches. The purity appears to be very high.

REDACTED



REDACTED

89

Ran a spectrum of  $\text{Co}$  in benzene.  $\rightarrow$  See attached page -  
Satellites

Came to lab about 3:00 P.M. Tried various  
solvents for  $\text{Co}$ . Successes with  $\text{CS}_2$  and  $\text{CCl}_4$  with a moderate  
apparent success for benzene. Failures included water,  
acetone, ethanol, methanol, propanol.

